A mixed basis approach in the SGP-limit

Matias Nordin[☆a], Martin Nilsson-Jacobi[b], Magnus Nydén[a]

[a] Applied Surface Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden
[b] Complex Systems Group, Department of Energy and Environment, Chalmers University of Technology, 412 96 Gothenburg, Sweden

Abstract

A perturbation method for computing quick estimates of the echo decay in pulsed spin echo gradient NMR diffusion experiments in the short gradient pulse limit is presented. The perturbation basis involves (relatively few) dipole distributions on the boundaries generating a small perturbation matrix in $O(s^2)$ time, where s denotes the number of boundary elements. Several approximate eigenvalues and eigenfunctions to the diffusion operator are retrieved. The method is applied to 1-D and 2-D systems with Neumann boundary conditions.

Keywords: NMR, SGP-limit, narrow pulse approximation, restricted diffusion, initial slope, matrix formulation, Laplace operator, perturbation method, geometry, Poisson's equation

1. Introduction

NMR-methods provide an arsenal of tools to study restricted diffusion [1, 2, 3] where not only mass transportal properties such as flow and diffusion can be studied [4, 5, 6, 7] but also characteristics of the material [8, 9, 10, 11]. Commonly used for diffusion studies is the pulsed gradient spin-echo (PGSE) NMR technique where the particle positions are labeled by a magnetic field gradient [12]. Position labeling is commonly performed by finite-length magnetic field gradient pulses and the theory for this experiment is described by the Bloch-Torrey equations [13]. In the short time gradient limit however, the spin-echo decay simplifies to a Fourier transform over the propagator [3]. The short time gradient approximation (SGP) is commonly used to describe the diffusion process when the geometric length scales of the material are longer that the effective gradient length scales as given in the q-vector approach [14, 15, 16, 17]. In heterogeneous materials the spin-echo decay normally results in a function that can be describe by a sum of exponentially decaying functions resulting in a rather featureless form. However, in structurally well-defined materials, such as packed mono-disperse micrometer sized beads it can display detailed features from which material structure details can be obtained [18, 19, 20, 11, 14, 21]. In addition, in the limit of short gradient pulses, the initial slope of the spin-echo decay always conveys information of the mean square displacement independent on material homogeneity/heterogeneity. It is thus of interest to calculate a spin-echo decay from homogeneous and heterogeneous materials in order to learn more about the dependence between material structure and diffusion. The naive approach to calculate the echo decay in the SGP-limit is done by diagonalizing the diffusion operator. In this paper we develop a perturbation technique to calculate rough, but quick estimates of the echo decay, based on approximate eigenfunctions of the diffusion operator. These approximate eigenfunctions separates free diffusion and the influence of the material. Interesting features of the material can thus be analyzed in detail, also for large scale systems.

2. Theory

In the short gradient pulse approximation the echo decay is described by the so called master equation, a Fourier transform over the propagator [6, 12, 22]

$$E(q,t) = \frac{1}{V}\langle q|P(r,r',t)|q\rangle \tag{1}$$

where by the volume term $\frac{1}{V}$ we have assumed that the initial positions of the particles are equally distributed among the sample and $\langle q| = e^{i2\pi qz}$, where q is a real and the applied gradient is in the z-direction. The propagator in equation 1 denotes the ordinary diffusion propagator [22], which can be expanded in eigenfunction/eigenvalue pairs [23, 22] as

$$P = \sum_{i=0}^{\infty} |i\rangle\langle i|e^{-t\lambda_i}.$$

The eigenequation for the eigenfunction/eigenvalue pairs is written as

$$L|i\rangle = \lambda_i|i\rangle \tag{2}$$

where L denotes the effective diffusion operator associated with the boundary conditions, which will be defined in detail below. Note that the master equation (equation 1) can be written as

$$E(q,t) = \frac{1}{V}\sum_{i=0}^{\infty} e^{-t\lambda_i}|\langle q|i\rangle|^2 \tag{3}$$

[☆] Corresponding author. Fax: +46 31160062
Email address: matias@chalmers.se (Matias Nordin[☆])

i.e. the echo decay is defined by the overlap between incoming modes $\langle q|$ and the eigenfunctions $|i\rangle$ to the diffusion operator L, weighted by the time-dependent term $e^{-t\lambda_i}$. In general, equation 3 must be solved using numerical methods, since the eigenfunctions of the diffusion operator are known only for simple geometries. We note also that for periodic boundary conditions the incoming mode $\langle q|$ is an harmonic function e.g an eigenfunction to Δ when q is an integer.

We write the diffusion operator as

$$L = \Delta - S \tag{4}$$

where Δ denotes the ordinary Laplace operator and S denotes an operator defining the boundary conditions. We will refer to S as the surface operator. We note that the unperturbed problem reduces to Laplace equation with solutions $\langle q|$ if q is a valid wave number [24] and it is evident that part of the perturbation basis need to consist of a set of integer valued $\langle q|$, for a correct solution in absence of S. By the form of equation 3 we are motivated to find some set of functions orthogonal to $\langle q|$ describing the influence of the surface operator S. The eigenfunctions of the diffusion operator would then be approximated by linear combinations of $\langle q|$ and these unknown vectors. The echo decay in equation 3 would then reduce to

$$E(q_i, t) \approx \frac{1}{V} e^{-t\lambda'} |\alpha_{q_i}|^2, \tag{5}$$

for weights α_{q_i} induced by the surface operator S. For simplicity we will omit the index i. λ' denotes the approximate eigenvalues of L. Such a construction will now be explained in detail.

We construct S by assuming Neumann conditions at the boundary Ω

$$\hat{n} \cdot \nabla\phi(\omega \in \Omega, t) = 0, \tag{6}$$

for the (unknown) solution $\phi(r, t)$. The operator S equals $\hat{n} \cdot \nabla$, and acts as a directional derivative on Ω. Each eigenfunction of S consist of two $\delta(r-\omega)$-functions with sign change over Ω and it is clear that standard perturbation techniques will not work, as the norm of S is large in the Laplace basis. By the form of the eigenfunctions to S we will refer to them as dipoles. Now we Fourier expand the eigenspace of S, with sign change over Ω to preserve the dipole form and denote such surface Fourier modes by σ_s. If the surface is smooth, a Fourier expansion on the boundary captures incoming waves $\langle q|$ of about the same wave numbers. This means that for a truncated set of Fourier modes $\{\langle q|\}_{q=1}^{N}$ in the low q-regime, a set of low wave-number surface modes suffices. We denote the number of such surface modes by M. The corresponding surface functions $|s\rangle$, are then calculated by solving Poisson's equation

$$|s\rangle = \int_{\Omega} \frac{1}{|r-\omega|} \sigma_s(\omega) d\omega \tag{7}$$

where in two dimensions the kernel is replaced by $\log |r - \omega|$. The approximate solutions to the diffusion problem (equation 2) can then be written as linear combinations of eigenfunctions to the Laplace operator Δ, $|q\rangle$ and solutions $|s\rangle$ to Poisson's equation (equation 7)

$$|i\rangle = \sum_{q}^{N} \alpha_q |q\rangle + \sum_{s}^{M} \beta_s |s\rangle. \tag{8}$$

This linear combination does not bear sense if $N \to \infty$, as of course $\{\langle q|\}_{q=0}^{\infty}$ already form complete set. If we however restrict ourselves to a subset of eigenfunctions of Δ, $N < \infty$, the complementary basis spanned by $|s\rangle$ is interesting and proposes a perturbation technique[1]. The outline of the mixed basis approach can also be found in[25].

Although the surface distributions $\sigma_s(\omega)$ are chosen to be orthogonal, the corresponding $|s\rangle$ will not be, but more importantly they nor will be orthogonal to $\langle q|$. The orthogonalization is however straight forward noting that

$$\langle q|s\rangle = \frac{1}{\lambda_q} \langle q|\sigma_s\rangle,$$

since Δ is self-adjoint. The scalar product between two solutions to Poisson equation is also involved in the orthogonalization, but can be treated as follows

$$\begin{aligned} \langle s|s'\rangle &= \int \int \frac{\sigma_s(\omega)}{|r-\omega|} d\omega \int \frac{\sigma_{s'}(\omega')}{|r-\omega'|} d\omega' dr \\ &= \int \sigma_s(\omega)\sigma_{s'}(\omega')\Theta(\omega,\omega') d\omega d\omega'. \end{aligned}$$

The interchange of the integration variables is valid provided that the unit cell is neutral [26] and the resulting function $\Theta(\omega, \omega')$ can be pre-calculated! Importantly the function Θ only depends on the unit cell size and number of dimensions and thus needs only to be calculated once and used as a look-up table. Furthermore, by noting that both

$$(\Delta - S)|s_\perp\rangle$$

and

$$(\Delta - S)|q\rangle$$

only need to be calculated over the surface, the resulting perturbation matrix is quickly accessible and is of size $(N + M) \times (N + M)$. The perturbation matrix has the following form

$$A_{i,j} = \langle i|(\Delta - S)|j\rangle,$$

where i and j range over all perturbation vectors i.e. $\{\langle q|\}_{q=1}^{N}$ and $\{\langle s_\perp|\}_{s=1}^{M}$. The scalars α_q in equation 5 as well as the approximate eigenvalues can be retrieved by diagonalization of the small perturbation matrix A. We denote the eigenfunctions of the perturbation matrix by $|k\rangle$. For $t \to 0$, the echo decay is solely expressed by $|\langle q|k\rangle|^2$ and can directly be read out from the first N elements of the diagonal of the perturbation matrix. Note also that when $t \to \infty$ the echo decay reduces to the first column of the perturbation matrix.

[1] This restriction also connects naturally with the experimental NMR setup, where the range of q-vectors is not complete but restricted by the gradient strength available.

3. Results

The perturbation basis has been validated in several trivial and non-trivial domains with good results. Three examples are presented here and in all examples the free space diffusion constant is set to unity.

The first example consists of diffusion between two plates separated by a distance a, a well studied situation for which an analytic expression is known [27, 15, 28]. A standard finite difference approach is used with a grid spacing $h = a/50$. The perturbation basis consist of $N = 10$ eigenfunctions to the Laplace operator Δ, and one dipole function representing the boundary ($M = 1$). The echo decay is shown in figure 1 for $t = 100$ and $t = \infty$ together with the real SGP-signal calculated from the eigenfunction expansion of L and the analytical infinite time solution $E(q, t \to \infty) = |\mathrm{sinc}(\pi q l)|^2$ [2]. The relative error of the approximate echo decay is of order $\sim 10^{-4}$ for this perturbation basis and relative error of the apparent diffusion constant, estimated from the initial slope of the echo decay [29], is also of order $\sim 10^{-4}$.

The following two examples consist of two-dimensional systems using $4 \cdot 10^4$ grid points. Periodic boundary conditions are used on the computational cell, which has a side length $l = 200$. Neumann boundary conditions separate the void space (white regions) and the structure (grey regions) and the echo decays are calculated in the void space. The dipole distributions for the boundaries are calculated by diagonalizing the finite difference approximation on the boundary yielding Fourier modes spanning the surface and sign change over the domain preserve the dipole form. The first such example consist of randomly distributed discs with equal radius (see figure 2). Figure 3 shows the real and approximate echo decays for times $t = 200, 900, 2000$ which are chosen to double the diffusive length in each step. The real echo decay is calculated with equation 3 using the 280 first eigenfunctions/eigenvalues to L, which gives an error $< 10^{-9}$ for $t > 200$. The approximate echo decay is calculated using the first $N = 150$ eigenfunctions to Δ and 20 surface Fourier modes per disc are used, in total $M = 280$ surface functions represent the boundaries. The relative error of the echo decay is of order $\sim 10^{-3}$.

The last example consists of diffusion in a more interesting 2-dimensional model. The model is generated by a parent/child process [30], where parents are created randomly using a uniform distribution and children are distributed around each parent using a Gaussian distribution. The pixel positions of the children then represent the material. The number of parents/children and the distribution parameters can be varied and the space of geometries is rich. Although such geometries work well in discrete case, they can of course not be spanned by Fourier modes in the continuous limit. Figure 4 shows an example of one such geometry and echo decays calculated for times $t = 200, 900, 2000$. The perturbation matrix is calculated using the $N = 100$ first eigenfunctions to Δ and $M = 100$ surface vectors. In the calculation of the real echo decay the first 230 eigenfunctions corresponding to the void space are used, which gives an error of order $< 10^{-9}$ for $t > 200$. The relative error of the approximative echo decay is of order $10^{-}2$.

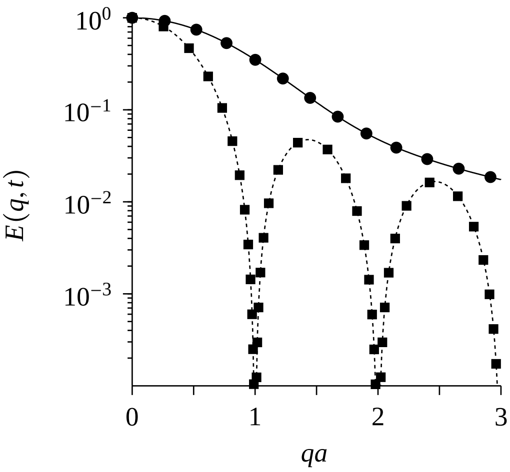

Figure 1: The figure shows echo decays for diffusion between two plates, separated by distance a. The real echo decay is calculated using equation 3 with the full spectrum of the diffusion operator L for time $t = 100$ (•). The approximate echo decay for the corresponding time is calculated using $N = 10$ eigenfunctions to the Laplace operator Δ and $M = 1$ surface function (solid line). Also shown is the infinite time solution $E(q, \infty) = |\mathrm{sinc}(\pi q l)|^2$ (■) and the approximate infinite time solution (dashed line) using the same perturbation basis as for the $t = 100$ signal. The approximate signals coincide well with expected results (the relative error is of order 10^{-4}).

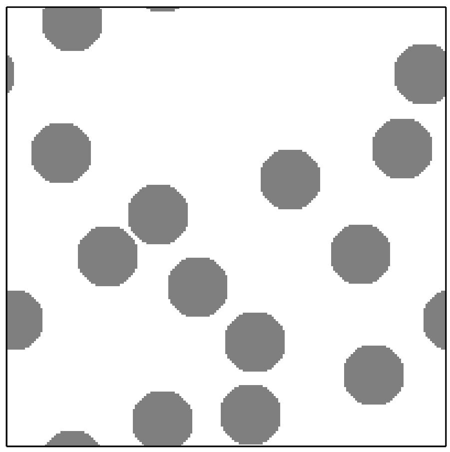

Figure 2: The figure shows a 2D-system consisting of randomly distributed discs of equal radius. The system consist of $4 \cdot 10^4$ grid points and Neumann boundary conditions separates the void space (white region) from structure (grey region). Figure 3 shows the real and approximate echo decay for different times.

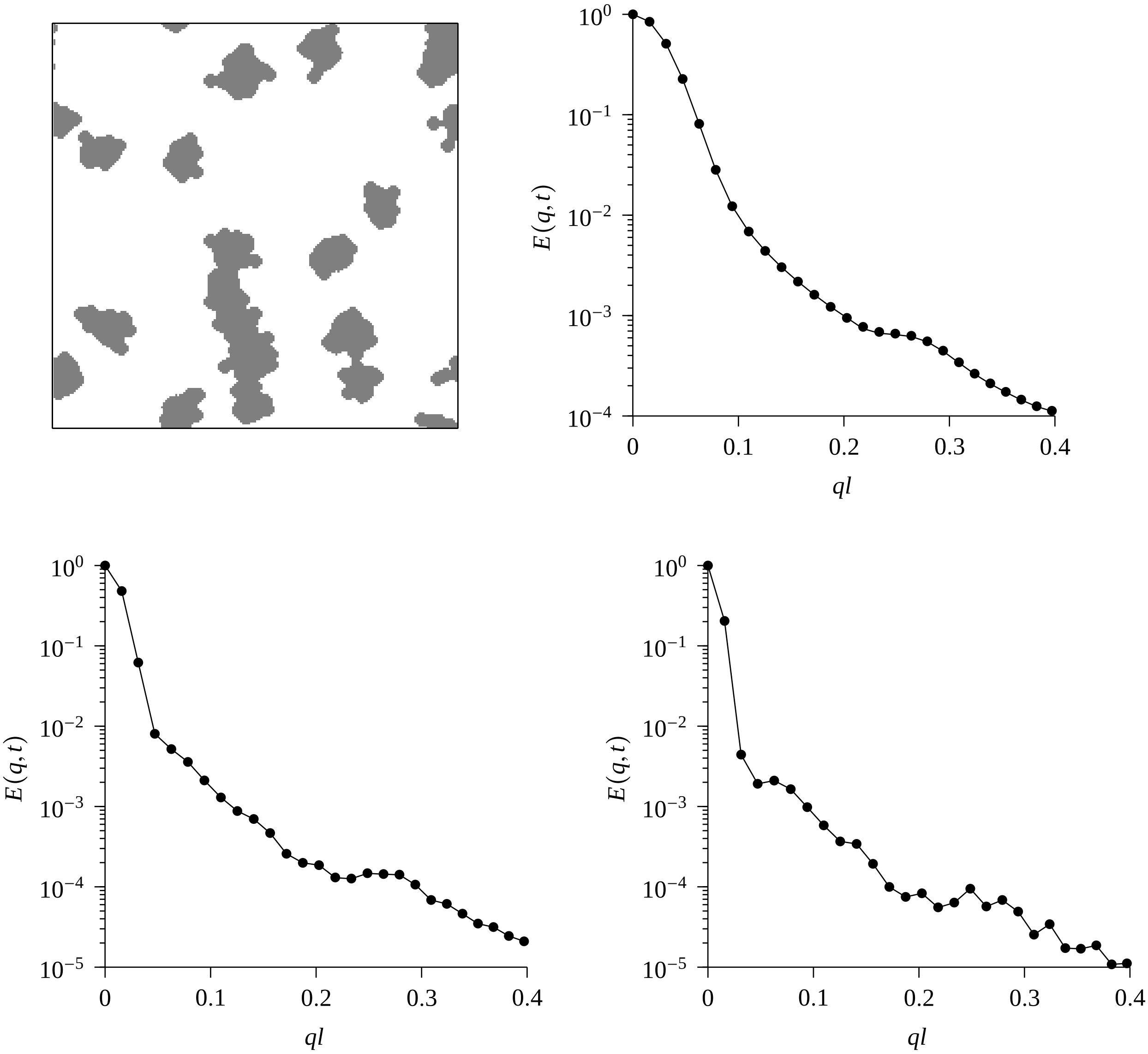

Figure 4: Echo decays for the model shown in top left image for times $t = 200$ (top right), $t = 900$ (bottom left) and $t = 2000$ (bottom right). The times are chosen to approximately double the diffusive length for each step. The real echo decay $E(q,t)$ is calculated using equation 3 (•) and the approximative echo decay is calculated using $M = 100$ surface functions and the first $N = 100$ eigenfunctions of Δ (solid line). Note that the approximative echo is calculated only at the corresponding q-values but the solid line is drawn between these, for visualization. $l = 200$ denotes the box side length. The relative error of the approximative echo decay is of order $\sim 10^{-2}$.

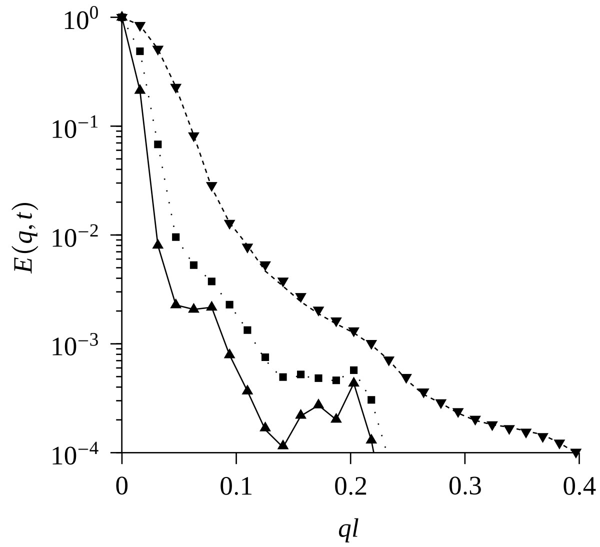

Figure 3: The figure shows echo decays for the 2D-example of randomly distributed discs (see figure 2). The real echo decay (calculated using equation 3) is shown for times $t = 200$ (▼), $t = 900$ (■) and $t = 2000$ (▲). The approximate echo decay is calculated using $N = 150$ eigenfunctions to the Laplace operator Δ and $M = 280$ surface functions and is shown for $t = 200$ (dashed line), $t = 900$ (dotted line) and $t = 2000$ (filled line). The box side length is $l = 200$. The times are chosen to approximately double the diffusive length for each time and the relative error of the approximate echo decays is of order $\sim 10^{-3}$. Note that the approximative echos are calculated only at the corresponding q-values but lines are drawn between these, for visualization.

4. Conclusions

We have shown that for diffusion problems with Neumann boundary conditions the echo decay in the SGP-limit can be calculated via a perturbation method with a mixed basis. Approximate echo decays are presented together with analytic and real echo decays (calculated from the eigenfunction expansion of the diffusion operator) for trivial and non-trivial geometries and the relative error of the echo decay is small. The mixed basis consist of (analytically known) eigenfunctions to the Laplace operator and solutions to Poisson's equation with dipole distributions on the boundary. Relatively few base vectors are needed for good result, resulting in a quickly accessible perturbation matrix. The method is formulated on the boundary, apart from a volume dependent function, which however is geometry independent and can be pre-calculated using standard Ewald summation techniques, saved to disk, and used as a lookup table for arbitrary geometries. This reduces the calculations of approximate propagators and/or echo decays in the SGP-limit to a computational complexity of $O(s^2)$, where s is the number of surface elements.

As the approximate eigenfunctions not fully compensate for the Neumann conditions on the boundaries a resonance effect has been observed when using harmonic functions in the perturbation basis with wave-lengths corresponding to the structure domains (grey regions), this increases the error of the echo decay at q-values corresponding to such wave lengths. At such wave lengths the approximate eigenfunctions consist of linear combinations of eigenfunctions corresponding to the outer (white region) and inner (grey regions) domains. This effect can be minimized by increasing the number of surface modes M, preserving the orthogonality to the inner domains and or not introduce harmonic functions at the resonance points. Note that the error due to this resonance effect is of the same order as the error at other q-values in the geometries presented, but more pronounced.

The method share similarities with other methods formulated on the boundary such as the boundary element methods [31] (BEM), analytic element methods [32] (AEM) and boundary approximation methods [33, 34] (BAE), also known as Trefftz methods, but might be an alternative due to the small size of the resulting perturbation matrix achieved in $O(s^2)$ time where s is the number of boundary elements. The approximate signals can also be improved by using the approximative eigenfunctions/eigenvalues as an initiator for other iterative method as for example [35] which relies on an initial guess of the eigenvalues. The mixed basis approach can also be extended from the SGP-limit to cover time-dependent gradients using the matrix formulation developed by Callaghan [36] based on a multiple propagator approach [37]. As the standard methods for calculations of the diffusion propagator are impractical for large-scale systems, due to the heavy computational demand, the mixed basis approach is suggested as a realistic tool for calculating approximative echo decays, also for finite gradients.

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